

Exercise 8

Problem 1:

In a process at your plant, you are mixing two liquids: benzene (1) and 2-propanol (2). You would like to create a molar enthalpy vs. composition diagram for this mixture and have found molar enthalpy of mixing data available in Table 1.

You may use Excel to plot the diagram and show the computation results of molar enthalpy for all compositions at $T = 298.15\text{K}$ and $T=308.15\text{K}$. Given:

$$C_{p,1} = 135.69 \frac{\text{J}}{\text{mol}} \cdot \text{K}$$

$$C_{p,2} = 155.0 \frac{\text{J}}{\text{mol}} \cdot \text{K}$$

T = 298.15 K		T = 308.15 K	
ΔH (J/mol)	x_1	ΔH (J/mol)	x_1
0	0	0	0
232.2	0.0632	92.2	0.0213
518.8	0.1451	284.5	0.0668
789.9	0.2346	511.4	0.1237
986.2	0.3129	735.4	0.1856
1110.4	0.3734	925.2	0.244
1186.6	0.4192	1100.5	0.3069
1234.3	0.4509	1225.4	0.3606
1281.1	0.4933	1319.5	0.4099
1319.2	0.5511	1408	0.479
1328.4	0.618	1454.9	0.5349
1287.4	0.6941	1473.4	0.6036
1201.6	0.7614	1431.3	0.6869
1071.1	0.8222	1294.3	0.7788
906.3	0.8773	1064	0.8615
687.4	0.929	766.5	0.9245
418.4	0.9669	436.8	0.9664
161.1	0.9889	153.8	0.9893
0	1	0	1

Table 1: Molar enthalpy of mixing of benzene (1) + 2-propanol (2) system at 298.15 K and 308.15K

The enthalpy change is the enthalpy difference between the mixture, and partial properties of the components (hint sheet)

$$\underline{H}^{\text{mix}} = \underline{H}^{\text{ix}} - (x_1 \underline{H}_1 + x_2 \underline{H}_2)$$

We only know $\underline{\Delta H}^{\text{mix}}, x_1, T \Rightarrow$ must reformulate

$$\text{Binary mixture: } x_2 = 1 - x_1$$

$$\text{Choose } T_{\text{ref}} = 298.15 \text{ K}$$

$$\text{Choose } H_i(T_{\text{ref}}) = 0$$

$$\text{Assume } C_{p,i} = \text{const}$$

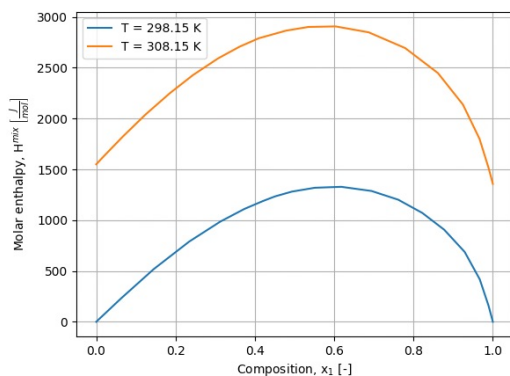
$$\Rightarrow H_i(T) = H_i(T_{\text{ref}}) + \int_{T_{\text{ref}}}^T C_{p,i} dT = C_{p,i}(T - 298.15 \text{ K})$$

Rearranging then gives:

$$\underline{H}^{\text{mix}} = \underline{\Delta H}^{\text{mix}} + (x_1 C_{p,1} + x_2 C_{p,2})(T - 298.15 \text{ K})$$

$$\Rightarrow \text{For } 298.15 \text{ K, } \underline{H}^{\text{mix}} = \underline{\Delta H}^{\text{mix}}$$

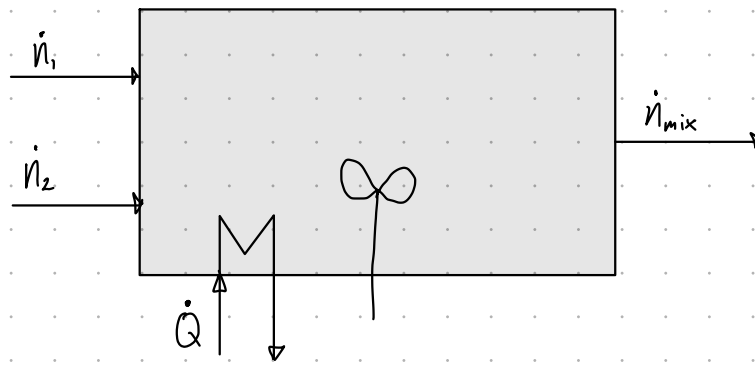
Inserting the data and the formula into python:



For T = 298.15 K			For T = 308.15 K		
dHmix [J/mol]	x1	Hmix [J/mol]	dHmix [J/mol]	x1	Hmix [J/mol]
0.0	0.0	0.0	0.0	0.0	1550.0
232.2	0.0632	232.2	92.2	0.0213	1638.1
518.8	0.1451	518.8	284.5	0.0668	1821.6
789.9	0.2346	789.9	511.4	0.1237	2037.5
986.2	0.3129	986.2	735.4	0.1856	2249.6
1110.4	0.3734	1110.4	925.2	0.244	2428.1
1186.6	0.4192	1186.6	1100.5	0.3069	2591.2
1234.3	0.4509	1234.3	1225.4	0.3606	2705.8
1281.1	0.4933	1281.1	1319.5	0.4099	2790.3
1319.2	0.5511	1319.2	1408.0	0.479	2865.5
1328.4	0.618	1328.4	1454.9	0.5349	2901.6
1287.4	0.6941	1287.4	1473.4	0.6036	2906.8
1201.6	0.7614	1201.6	1431.3	0.6869	2848.7
1071.1	0.8222	1071.1	1294.3	0.7788	2693.9
906.3	0.8773	906.3	1064.0	0.8615	2447.6
687.4	0.929	687.4	766.5	0.9245	2138.0
418.4	0.9669	418.4	436.8	0.9664	1800.2
161.1	0.9889	161.1	153.8	0.9893	1512.8
0.0	1.0	0.0	0.0	1.0	1356.9

Problem 2: Using molar enthalpy diagram for a solution

In a mixing unit at your plant, you mix 40 moles/min of an equimolar mixture of benzene(1) + 2-propanol (2) at 298.15 K with 80 moles/min of pure benzene at 298.15 K. If you desire to keep the resulting mixture at 298.15 K, what is the heat load on this system? Are you adding or removing heat?



$$\text{Benzene in: } \dot{n}_B = 0,5 \cdot \dot{n}_1 + \dot{n}_2 = 100 \text{ mol/min}$$

$$\text{2-propanol in: } \dot{n}_P = 0,5 \cdot \dot{n}_1 = 20 \text{ mol/min}$$

$$\text{Frac benzene in: } X_1 = \frac{100}{100+20} = 0,833$$

The complete energy balance

$$\frac{d}{dt} \left(m \left[\hat{U} + \frac{V^2}{2} + gh \right] \right) = \sum_{j=1}^{j=J} \left[\dot{m}_{j,in} \left(\hat{H}_j + \frac{V_j^2}{2} + gh_j \right) \right] - \sum_{k=1}^{k=K} \left[\dot{m}_{k,out} \left(\hat{H}_k + \frac{V_k^2}{2} + gh_k \right) \right] + \dot{W}_S + \dot{W}_{E/C} + \dot{Q}$$

- Assuming that the changes in kinetic and potential energy are negligible compared to the change in internal energy $\frac{V^2}{2} \approx 0, gh \approx 0$

- Steady state $\frac{d}{dt} \left(m \left[\hat{U} + \frac{V^2}{2} + gh \right] \right) = 0$

- No expansion/contraction or shaft work

$$\Rightarrow 0 = \dot{n}_1 \cdot \underline{H}_1 + \dot{n}_2 \cdot \underline{H}_2 - \dot{n}_{mix} \cdot \underline{H}^{mix} + \dot{Q}$$

$$\Rightarrow \dot{Q} = \dot{n}_{mix} \cdot \underline{H}^{mix} - \dot{n}_1 \cdot \underline{H}_1 - \dot{n}_2 \cdot \underline{H}_2$$

As $\dot{n}_2$ is pure benzene $\underline{H}_2 = 0$ (chosen reference state)

Using linear regression with $x_1 = 0,833$

$$H^{mix}(x_1 = 0,833) = H^{mix}(x_1 = 0,8222) + \frac{H^{mix}(x_1 = 0,8773) - H^{mix}(x_1 = 0,8222)}{0,8773 - 0,8222} \cdot (0,833 - 0,8222)$$

$$\underline{H^{mix}(x_1 = 0,833) = 1037,8 \text{ J/mol}}$$

Similarly, using $x_1 = 0,5$

$$\Rightarrow \underline{H_1 = 1285,5 \text{ J/mol}}$$

$$\dot{Q} = \dot{n}_{mix} \cdot \underline{H^{mix}} - \dot{n}_1 \cdot \underline{H_1} - \dot{n}_2 \cdot \underline{H_2}$$

$$\dot{Q} = 120 \text{ mol/min} \cdot 1037,8 \text{ J/mol} - 40 \text{ mol/min} \cdot 1285,5 \text{ J/mol}$$

$$\underline{\dot{Q} = 73116 \text{ J/min}}$$

This does not match the numerical solution, am I doing anything wrong?

$$\underline{\dot{Q} > 0 \Rightarrow \text{Adding heat}}$$

Problem 3: Using partial molar quantities

Suppose that the liquid molar enthalpy for a binary mixture of benzene (1) and cyclohexane (2) has been fit to the following functional form at 25°C and 1 bar. Thus,

$$\underline{H} = -3399 + 4516x_1 - 3215x_1^2$$

where $\underline{H}$ [=] J/mol.

- What is the partial molar enthalpy of benzene in this mixture when it is equimolar at 25°C and 1 bar?
- What is the partial molar enthalpy of cyclohexane in this mixture when it is equimolar at 25°C and 1 bar?
- What is the pure component molar enthalpy of cyclohexane at 25°C and 1 bar?

For a binary mixture, the following equations apply to partial molar quantities (here enthalpy)

$$\underline{H_1} = \underline{H_{mix}} + x_2 \frac{dH_{mix}}{dx_1} \quad \textcircled{1}$$

$$\underline{H_2} = \underline{H_{mix}} - x_1 \frac{dH_{mix}}{dx_1} \quad \textcircled{2}$$

Not sure if these should be proven or not, let me know if I should have.

A) From $\textcircled{1}$

$$\underline{H_1} = -3399 + 4516 \cdot 0,5 - 3215 \cdot 0,5^2 + 0,5 \cdot (4516 - 2 \cdot 3215 \cdot 0,5)$$

$$\underline{\underline{H_1 = -1294,25 \text{ J/mol}}}$$

B) From ②

$$\underline{H_2} = -3399 + 4516 \cdot 0,5 - 3215 \cdot 0,5^2 - 0,5 \cdot (4516 - 2 \cdot 3215 \cdot 0,5)$$

$$\underline{\underline{H_2 = -2595,25 \text{ J/mol}}}$$

C) From ②

As $x_1 = 0$, the derivative term is 0, using $x_1 = 0$ in the given expression for H gives:

$$\underline{\underline{H_2 = -3399 \text{ J/mol}}}$$

Problem 4:

Figure 1 drawn in Problem 1 describes the molar enthalpy for the benzene (1) + 2-propanol (2) system at two temperatures: 298.15 K and 308.15 K. Answer the following questions related to this figure.

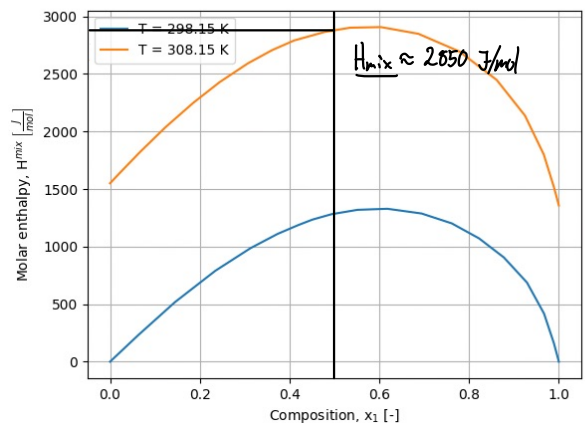
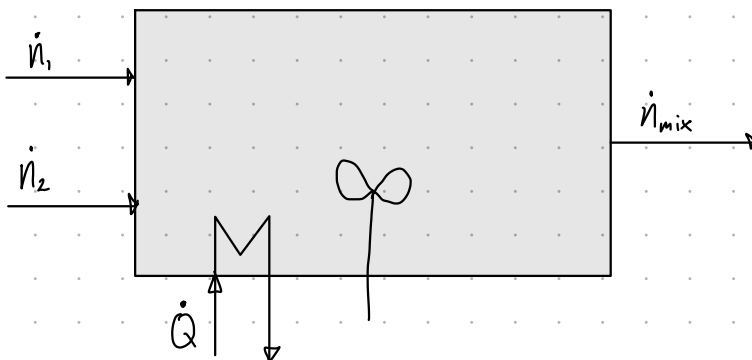
a) A flow process mixes 10 moles per second of benzene with 10 moles/s of 2-propanol at 308.15 K. Would this system give off heat, absorb heat, or stay at the same temperature? Please explain.

b) If you assume the benzene + 2-propanol mixture behaved as an ideal solution, how would your answer from part (a) change?

a) Here I will use a formula from problem 2

$$\dot{Q} = \dot{n}_{\text{mix}} \cdot \underline{H^{\text{mix}}} - \dot{n}_1 \cdot \underline{H_1} - \dot{n}_2 \cdot \underline{H_2}$$

Sketch:



Both n_1 and n_2 are pure components $\Rightarrow$ $\underline{H_1} = C_{p1} \Delta T = 135,69 \cdot 10 = 1356,9 \text{ J/mol}$
 $\underline{H_2} = C_{p2} \Delta T = 155 \cdot 10 = 1550 \text{ J/mol}$

$$\dot{Q} = 20 \cdot 2850 - (10 \cdot 1356,9 + 10 \cdot 1550)$$

$$\underline{\underline{\dot{Q} = 27931 \text{ W}}}$$

As $\dot{Q} > 0$, the system will absorb heat under these conditions

b) If this was an ideal solution, then $\underline{H}^{mix} = x_1 \underline{H}_1 + x_2 \underline{H}_2$

this means that $\dot{Q} = 0$

$\Rightarrow$ The system stays at the same temperature

$$\begin{aligned}\dot{Q} &= \dot{n}_{mix} \cdot \underline{H}^{mix} - \dot{n}_1 \cdot \underline{H}_1 - \dot{n}_2 \cdot \underline{H}_2 \\ \dot{Q} &= \dot{n}_{mix} \left(\underline{H}^{mix} - (x_1 \underline{H}_1 + x_2 \underline{H}_2) \right) \\ \dot{Q} &= 0 \quad \quad \quad = 0\end{aligned}$$

Problem 5:

The molar volume for a mixture of methanol (1) + water (2) at 298.15 K and 1 bar is given as:

$$\underline{V} = 18.102 + 18.491x_1 + 4.1506x_1^2$$

Where $\underline{V}$ is in units of cm^3/mol

a) What is the partial molar volume of methanol at this T and P when $x_1 = 0.4$?

b) What is the pure component molar volume of methanol at this T and P?

c) What is the pure component molar volume of water at this T and P?

d) Let's assume you have an equimolar mixture of water and methanol. What will be the molar volume of this mixture according to the functional form given in the problem? What will be the molar volume of this mixture if you assumed this mixture behaved as an ideal solution?

Similarly to problem 3,

$$\underline{V}_1 = \underline{V} + x_2 \frac{d\underline{V}}{dx_1} \quad (1)$$

$$\underline{V}_2 = \underline{V} - x_1 \frac{d\underline{V}}{dx_1} \quad (2)$$

$$a) \frac{d\underline{V}}{dx_1} = 18.491 + 8.3012x_1$$

$$(1) \underline{V}_1 = 18.102 + 18.491 \cdot 0.4 + 4.1506 \cdot 0.4^2 + 0.6 \cdot (18.491 + 8.3012 \cdot 0.4)$$

$$\underline{V}_1 = 39.249 \text{ cm}^3/\text{mol}$$

$$b) (1) \underline{V}_1 = 18.102 + 18.491 \cdot 1 + 4.1506 \cdot 1^2 + 0 \cdot (18.491 + 8.3012 \cdot 1)$$

$$\underline{V}_1 = 40.744 \text{ cm}^3/\text{mol}$$

$$c) (2) \underline{V}_2 = 18.102 + 18.491 \cdot 0 + 4.1506 \cdot 0^2 - 0 \cdot (18.491 + 8.3012 \cdot 0)$$

$$\underline{V}_2 = 18.102 \text{ cm}^3/\text{mol}$$

$$d) \underline{V} = 18.102 + 18.491 \cdot 0.5 + 4.1506 \cdot 0.5^2$$

$$\underline{\text{Functional form } \underline{V}} = 28.385 \text{ cm}^3/\text{mol}$$

Ideal solution $\underline{V} = \underline{V}_1 \cdot x_1 + \underline{V}_2 \cdot x_2$, using the answers from b) and c):

$$\underline{V} = 40.744 \cdot 0.5 + 18.102 \cdot 0.5$$

$$\underline{\text{Ideal solution } \underline{V}} = 29.423 \text{ cm}^3/\text{mol}$$